

Stabilisation of Emulsions by Trapped Species

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Abstract

We consider an emulsion whose droplets contain a trapped species (insoluble in the continuous phase), and study the emulsion's stability against coarsening via Lifshitz–Slyozov dynamics (Ostwald Ripening). Extending an earlier treatment by Kabalnov et al (*Colloids and Surfaces*, **24** (1987), 19-32), we derive a general condition on the mean initial droplet volume which ensures stability, even when arbitrary polydispersity is present in both size and composition of the initial droplets. We distinguish “nucleated” coarsening, which requires either fluctuations about the mean field equations or a tail in the initial droplet size distribution, from “spinodal” coarsening in which a typical droplet is locally unstable. A weaker condition for stability, previously suggested by Kabalnov et al., is sufficient only to prevent “spinodal” coarsening and is best viewed as a condition for metastability. The coarsening of unstable emulsions is considered, and shown at long times to resemble that of ordinary emulsions (with no trapped species), but with a reduced value of the initial volume fraction of dispersed phase. We discuss the physical principles relevant to the stability of emulsions with trapped species, describing how these may be exploited to restabilise partially coarsened emulsions and to “shrink” previously formed emulsion droplets to form “mini-emulsions”.

1 Introduction

A phenomenological model for the growth of small droplets or precipitates from a supersaturated phase, was first investigated by Lifshitz and Slyozov[1] in 1961. They considered a two-phase system consisting of a vanishingly small volume fraction of droplets of a dispersed phase, evenly distributed throughout a second, continuous phase. The model is extremely general and forms an explanation for a number of different physical phenomena. Among these is the coarsening of emulsion droplets made of a liquid of low but finite solubility in the surrounding continuous phase[2, 3, 4, 5, 6]. The Lifshitz–Slyozov model is based on a mean-field description of the evaporation/condensation process (Ostwald ripening), which ignores the contributions of *coalescence* (droplet fusion). Depending upon the nature of the local interactions between droplets, their mobility, and the solubility of the dispersed phase within the continuous one, this can

be a good approximate description of the coarsening of emulsion droplets. The effects of coalescence are ignored in this paper. The absence of coalescence may require the presence of surfactant to stabilize the emulsion droplets (for example by imparting a surface charge). We do not treat surfactant dynamics explicitly, assuming in effect that the surfactant transports rapidly through the continuous medium to ensure a constant surface tension of droplets at all times.

Recent work[7, 8, 9, 10] has considered how the process differs when there are (disregarding surfactant) three species present[2, 3, 4]. In particular, Kabalnov et al.[7] considered a limiting situation where the third species is completely immiscible with the continuous phase, and is therefore effectively *trapped* within droplets. Kabalnov et al. gave quantitative criteria for the stabilisation of an emulsion by trapped species under the condition that the initial droplets were narrowly distributed in both size and composition. Related ideas to these can be found in the literature on meteorology[11, 12, 13, 14, 15], where (for example) the stability of sea-mists and/or smog is in part attributed to the inhibition of coarsening by the entrapment of salt or other non volatile species.

In this paper, we consider the effects of trapping a third species within emulsion droplets in greater detail. (Although we speak only of emulsions, several of our ideas relating to the stabilisation of droplets and precipitates to coarsening may be useful in other contexts[15, 16, 17].) We reexamine the condition for stability proposed in Ref.[7], and conclude that this is, for monodisperse droplets, the requirement for *metastability*, rather than full stability. We give a more stringent condition for full stability, which allows for fluctuations about the mean-field growth rate of droplets of a given size. Our stability condition is then extended to the case of an arbitrary initial distribution of droplet sizes and compositions. We note that this stability condition generalises to nonideal equations of state, such as would be needed to describe trapped salt, for example. The classification of stable and metastable regimes is, for emulsions, somewhat different from the one which applies to a single droplet surrounded by vapour, as was studied (with a trapped species present) in Ref.[8].

These arguments, which are described in Sections 2-4, are both general and rigorous. Indeed, in the absence of coalescence processes, the problem of the stability of dilute emulsions with trapped species is found to be analogous to the finding of phase equilibrium in multicomponent mixtures. The only difference is that some extra thermodynamic variables are required, to describe the fixed number of droplets and their trapped contents. These variables would not be conserved if either coalescence were to occur, or the trapped species were able to diffuse through the continuous phase at a finite rate. (The latter case is briefly discussed, at the end of Section 4.) But if these processes are slow enough, our methods allow the state of the system, after the remaining degrees of freedom have attained equilibrium, to be determined.

In Section 5, we consider the effect of a trapped phase on the kinetics of coarsening, in a system which does not obey the criterion for stability derived earlier. Approximate solutions for the droplet size distributions are given, and the physically motivated approximations upon which they are based are explained. Our analysis supports the view of Ref.[7], that in the unstable (coarsening) growth regime, the long time dynamics is essentially the same as given by the Lifshitz Slyozov description.

In Section 6, several implications and possible applications of these results are considered, including possibly novel methods for forming stable emulsions of small

droplet size, and ways of arresting or reversing coarsening after it has already begun. Section 7 gives a brief conclusion and outlook for further work.

2 Kinetics of Droplet Growth

We consider a vanishingly small volume fraction of droplets and assume that droplets are in equilibrium with their local spatial environments. We also assume that the ensemble of droplets interacts via diffusion of the dispersed-phase species through the continuous medium, and that this diffusion is rate-limiting (it is much slower than the rate at which the dispersed-phase species may be absorbed into a droplet from immediately outside). Each droplet's growth rate is then determined by the difference in concentration of dispersed-phase species immediately outside its surface and the (average) far-field concentration within the continuous phase. These assumptions reduce the calculation to (i) a single body equilibrium problem, to find the mean growth rate of a droplet in terms of its size and the ambient supersaturation; and then (ii) a many-body problem to determine the droplet size distribution as a function of time. Since in stage (ii) each droplet interacts with the others only through the ambient supersaturation, the problem is tractable.

The method and assumptions just described are basically the same as those first used by Lifshitz and Slyozov[1] to obtain the average rate of droplet growth and an asymptotic solution for the droplet size distribution. Although other methods have been used to correct and improve those used by Lifshitz and Slyozov, the resultant corrections are small and the resulting asymptotic solutions essentially the same. For a clear exposition of the main ideas see Bray[18]. A review of recent theoretical and experimental work is given by Voorhees[19], and includes an overview of theoretical work on systems at finite droplet volume fractions.

2.1 Local Equilibrium of a Droplet

We treat all components of the emulsion as incompressible fluids, in which case the Helmholtz free energy of a dispersed-phase drop is given by

$$F_d = F_b + \sigma 4\pi R^2 \quad (1)$$

where F_b is the free energy of the same amount of bulk liquid, σ is the surface tension, and R is the droplets radius. This results in a chemical potential given by

$$\mu_d = \mu_b + \frac{2\sigma v_b}{R} \quad (2)$$

where v_b is the volume of a single molecule, and μ_b the chemical potential, in a bulk liquid of the dispersed phase.

Some of the dispersed-phase species does not reside in droplets but is instead molecularly dissolved in the continuous phase at concentration C . The chemical potential of such molecules is

$$\mu_c = \mu_{c0} + k_B T \ln C \quad (3)$$

where μ_{c0} is a reference value. (This assumes that the molecular solution is dilute enough to behave ideally.) At equilibrium $\mu_d = \mu_c$ so, immediately above a droplet

surface, the concentration $C(R)$ obeys

$$k_B T \ln(C(R)) = \frac{2\sigma v_b}{R} + \mu_b - \mu_{c0} \quad (4)$$

At a flat interface with radius of curvature $R \rightarrow \infty$, we have $k_B T \ln(C(\infty)) = \mu_b - \mu_{c0}$, so that we may write

$$C(R) = C(\infty) \exp\left(\frac{\Delta\mu}{k_B T}\right) \quad (5)$$

where μ_{c0} has been eliminated and

$$\Delta\mu = \mu_d - \mu_b = \frac{2\sigma v_b}{R} \quad (6)$$

For small values of $\Delta\mu/k_B T$, as are generally maintained during the late stages of the coarsening process, we may expand Eq.5 to obtain

$$C(R) \simeq C(\infty) \left(1 + \frac{2\sigma v_b}{k_B T R}\right) \quad (7)$$

In fact, for typical emulsion systems near room temperature with interfacial tensions $\leq 10^{-1} \text{Nm}^{-1}$ and initial droplets $\sim 0.1 \mu\text{m}$ or larger in size (as would arise for emulsions made by mechanical agitation) the approximation $\Delta\mu/k_B T \ll 1$ is likely to be valid throughout the coarsening process.

2.2 Rate of Droplet Growth

Under the conditions studied here \bar{c} , the average concentration of dispersed-phase species dissolved in the continuous phase, will itself be close to $C(\infty)$. Hence the reduced supersaturation of dispersed-phase species, which we define as

$$\epsilon = (\bar{c} - C(\infty))/C(\infty) \quad (8)$$

will be small. This means that droplet sizes change slowly on the time scale of relaxation of the diffusion field: a steady-state approximation may then be made for the concentration profile around a droplet. This entails replacing the diffusion equation $\partial c/\partial t = D\nabla^2 c$ with $\nabla^2 c = 0$. Imposing as boundary conditions $c(R) = C(R)$ (the equilibrium value at the droplet surface) and $c(\infty) = \bar{c}$ (the mean value far away), we obtain the steady-state profile

$$c(r) = R \left(\frac{C(R) - \bar{c}}{r} \right) + \bar{c} \quad (9)$$

for the concentration field $c(r)$ at a distance r from the centre of a droplet of radius R .

Since we assume that the process is diffusion-limited, the rate of droplet growth at the surface is given by the incident flux as

$$\frac{dR}{dt} = v_b D \left. \frac{\partial c}{\partial r} \right|_R = v_b D \left(\frac{\bar{c} - C(R)}{R} \right) \quad (10)$$

Using the linearised form (7) for $C(R)$ we obtain

$$\frac{dR}{dt} = \frac{Dv_b C(\infty)}{R} \left(\epsilon - \frac{2\sigma v_b}{k_B T R} \right) \quad (11)$$

If we define reduced variables $R' = Rk_B T / (2\sigma v_b)$, $t' = tDC(\infty)k_B^2 T^2 / 4v_b \sigma^2$ and a reduced growth rate $U(R', \epsilon) = dR'/dt'$ then Eq.11 simplifies to [18]

$$U(R', \epsilon) = \frac{\epsilon}{R'} - \frac{1}{R'^2} \quad (12)$$

This shows the balance between condensation (first term) and the evaporation driven by the Laplace pressure effect (second term). Note that no finite droplet size can be stable against evaporation at long times, when the supersaturation ϵ tends to zero. Accordingly, emulsion droplets of a single species with finite diffusivity will always coarsen.

3 The Effect of a Trapped Species

Molecules of a third species which are entirely immiscible with the continuous phase, are now considered to be present within droplets. Such molecules are effectively *trapped*. This has the immediate consequence that no droplet of the dispersed phase can ever entirely evaporate. So the trapped phase results in the additional thermodynamic constraint that the *total number of droplets* remains constant in time, with a value determined by the initial conditions.

We assume for simplicity that the trapped species may be treated as dilute within each droplet. (This assumption is relaxed in Section 4.7 below). In this case an additional term which corresponds physically to the osmotic pressure of the trapped phase, will contribute to the droplets chemical potential. Indeed it is easily confirmed [7] that Eq.6 is modified to

$$\Delta\mu = \left[\frac{2\sigma}{R} - \frac{\eta k_B T}{(4/3\pi)R^3} \right] v_b \quad (13)$$

where η is the number of trapped particles in the droplet. Thus, the osmotic pressure of the trapped species (second term) competes directly with the Laplace pressure (first term); the latter favours fewer, larger droplets whereas the osmotic pressure favours a uniform droplet size (at least if all droplets have the same η).

Note that the second term diverges as $R \rightarrow 0$; although the trapped species cannot be treated as dilute in this limit, the above formula is already enough to prevent a droplet from ever evaporating completely. Using Eq.13 to determine a growth rate dR/dt we find that Eq.11 becomes

$$\frac{dR}{dt} = \frac{Dv_b C(\infty)}{R} \left(\epsilon - \frac{2\sigma v_b}{k_B T R} + \frac{\eta v_b}{(4\pi/3)R^3} \right) \quad (14)$$

When $\eta = 0$, a characteristic length scale R_ϵ can be defined by

$$R_\epsilon = \frac{2\sigma v_b}{\epsilon k_B T} \quad (15)$$

which gives a critical size above which droplets will grow in size and below which droplets will dissolve. When $\eta > 0$ we may define another characteristic length scale R_B by that at which the osmotic and Laplace pressures are in balance, which gives

$$R_B = \left(\frac{3\eta k_B T}{8\pi\sigma} \right)^{1/2} \quad (16)$$

Hence the growth rate may be written in the more informative manner

$$\frac{dR}{dt} = \frac{Dv_b^2 C(\infty) 2\sigma}{Rk_B T} \left(\frac{1}{R_\epsilon} - \frac{1}{R} + \frac{R_B^2}{R^3} \right) \quad (17)$$

As shown in figure 1, when $\eta > 0$ a second zero at $R \sim R_B$ is introduced into the growth rate in addition to the original one. The stability of the new fixed point at $R \sim R_B$ suggests the possibility of forming stable emulsions; but since the curves depend on ϵ , which is time-dependent and need not even tend to zero at long times, the ultimate behaviour of the system is unclear. This is considered further in the following Section.

It is possible to define a growth velocity $U(R', \epsilon)$ in terms of dimensionless variables, as

$$U(R', \epsilon) = \frac{\epsilon}{R'} - \frac{1}{R'^2} + \frac{R_B'^2}{R'^4} \quad (18)$$

where R', t' are as defined in Section 2 above, and $R_B'^2 = 3\eta k_B^3 T^3 v_b / 32\pi\sigma^3$. This form of the growth rate is used in Section 5 when considering the dynamics of unstable distributions which coarsen.

4 Formation of Stable Emulsions

In discussing stability criteria, we assume a monodisperse initial condition with an ideal equation of state for the trapped species within the droplets. These assumptions will be relaxed in Sections 4.5 and 4.7 below.

4.1 Equilibrium at Fixed Droplet Number

Consider an initially monodisperse emulsion in which the number of trapped particles η is identical in each droplet. Since the emulsion droplets are treated as macroscopic objects their entropy of mixing is negligible, and may be ignored. The total free energy density of the system, at some later time, may be then written

$$F = \int dV n(V) f(V, \eta) \quad (19)$$

where $n(V)$ is the number density of droplets of volume V and $f(V, \eta)$ is the free energy of such a droplet containing η trapped molecules. For an ideal trapped species, $f(V, \eta)$ takes the form

$$f(V, \eta) = \mu_b V / v_b + 4\pi\sigma(3V/4\pi)^{2/3} - \eta k_B T \ln V \quad (20)$$

where a constant has been suppressed. The curves with and without trapped species are shown in figure 2.

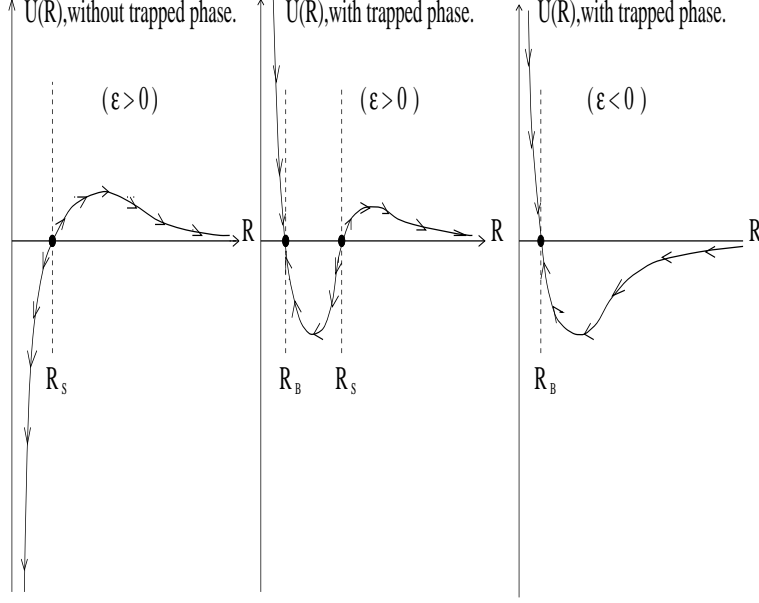


Figure 1: A schematic diagram representing how the presence of a trapped phase introduces a stable droplet size. Droplets of a given size move in the direction shown by the arrows. Without trapped species there is one unstable fixed point at R_S . With a trapped species a new, stable, fixed point appears at R_B due to the competition between Laplace and osmotic pressure. If there are trapped species and ϵ is negative then there is again only one fixed point, but it is the stable one at R_B . Formulae for R_S , R_B appear in Section 4.2 below.

The free energy density F is to be minimised subject to the constraints that $\int dV n(V) = n_0$ (the initial number of droplets is held constant), and $\int dV V n(V) = \phi = n_0 \bar{V}$, representing a fixed total volume fraction ϕ of dispersed phase[20]. The latter ignores a contribution from the dispersed-phase species that is solubilized in the continuous phase; for emulsions of low solubility, prepared by mechanical dispersion (rather than by quenching from a homogeneous mixture at high temperatures) the latter is always negligible. Note that the linear term, $\mu_b V/v_b$ in $f(V)$ is irrelevant to this procedure and, for clarity, we have subtracted it from the curves shown in Fig.2 and similar curves appearing below.

These rules are precisely analogous to those for constructing the equilibrium state of a system whose free energy $f(\lambda)$ depends on a composition variable λ . Such a system can separate into volumes $v(\lambda)$ of phases with different compositions λ ; in that case, $F = \sum_{\lambda} v(\lambda) f(\lambda)$ is minimised subject to the constraints $\sum_{\lambda} v(\lambda) = v_0$ (the total volume of the system is fixed) and $\sum_{\lambda} v(\lambda) \lambda = v_0 \lambda_0$ (the total amount of species λ is conserved). Here the subscripts 0 describe a hypothetical homogeneous state.

In this analogy, each value of the droplet size V corresponds to a “phase” of the system, and $n(V)$ corresponds to the “volume” of such a phase present in the final state. A monodisperse emulsion represents a “single phase”. The minimisation of F is therefore exactly as one would perform to find phase equilibrium in a binary fluid with the function $f(\lambda)$ replacing $f(V, \eta)$: the usual construction for this is to seek

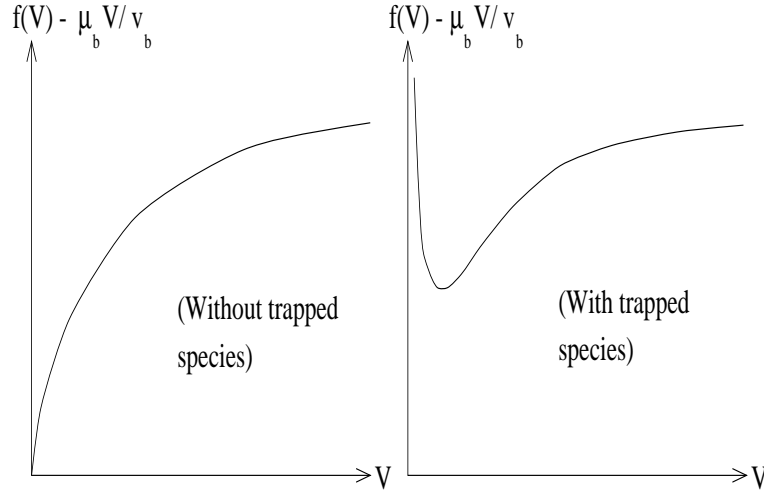


Figure 2: Comparison of curves of $f(V) - \mu_b V/v_b$ without (left) and with (right) trapped species.

common tangencies whereby F can be lowered by phase separation. (In this analogy, phase separation corresponds to the formation of droplets of more than one size.) The volumes $v(\lambda)$ are determined by the lever rule[21], and, in principle, the same rule would apply here to calculating $n(V)$ under conditions where more than one droplet size was present in equilibrium. Notice that the correspondence works only for the curve $f(V, \eta)$; no similar construction applies to $f(R, \eta)$, which is the form more usually considered in the literature [7, 8]. Also, note that any prediction of a “single phase” (*i.e.*, a monodisperse emulsion) is, in principle, subject to a small spreading of the size distribution arising from the entropy of mixing of the emulsion droplets themselves (rather than of the contents within one droplet), which we have neglected.

4.2 Stability Criterion for Monodisperse Emulsions

According to the above argument, if η is the same for all droplets (as will usually be nearly true if the initial droplet distribution is monodisperse) the equilibrium state of the system at fixed droplet number can be found by inspection of the $f(V, \eta)$ curve. A monodisperse emulsion can be stable only if the corresponding V lies in a part of the curve of positive curvature; if this is not the case then the free energy may be reduced (at fixed total number of droplets and fixed η in each drop) by the monodisperse distribution becoming polydisperse, and coarsening will occur. However, though necessary for stability, positive curvature is not sufficient to prevent coarsening, since even when the curvature is positive at a point $V = V_0$, it may be possible to find a lower free energy by constructing a common tangent on the $f(V)$ curve which lies below $f(V_0)$. The shape of the $f(V)$ curve shown in figure 2 dictates that any such tangency must connect the point at $V \rightarrow \infty$ to the absolute minimum of $f - \mu_b V/v_b$; the latter arises at $V = V_B(\eta)$ and is discussed further below.

The weaker of the two stability conditions (positive curvature) is precisely that

given by Kabalnov et al[7]:

$$V \leq V_S(\eta) = \left(\frac{3\eta k_B T}{2\sigma} \right)^{3/2} \sqrt{\frac{4\pi}{3}} \quad (21)$$

Hence Kabalnov et al[7] reasoned that a sufficiently monodisperse initial distribution with droplet size $V_0 < V_S \equiv 4\pi R_S^3/3$ would be stable. However, the above argument shows this is actually a criterion for metastability. In other words, the criterion of Ref.[7] actually separates initial distributions which coarsen immediately, from those where coarsening requires some fluctuation to bring it about. Since every droplet has a slightly different environment, such fluctuations are invariably present, though they are not included within the theory of Lifshitz and Slyozov. The kinetic mechanism for fluctuation-induced coarsening is discussed in the following Section 4.3. The extent of the metastable region, and the likelihood of a suitable fluctuation actually occurring, are discussed further in Section 4.6.

In any case, the above thermodynamic analogy shows that full stability in fact arises for initially monodisperse emulsions if and only if

$$V_0 \leq V_B(\eta) = \left(\frac{\eta k_B T}{2\sigma} \right)^{3/2} \sqrt{\frac{4\pi}{3}} \quad (22)$$

This corresponds to the requirement that the initial state lies to the left of the absolute minimum in the function $f(V, \eta) - \mu_b V/v_b$. Everywhere to the right of this minimum, a lower global free energy can be constructed by a common tangency between V_B and (formally) $V = \infty$. This corresponds to a final, coarsened state in which a monodisperse emulsion of droplet size $V_B = 4\pi R_B^3/3$ and droplet number density n_0 coexists with an “infinite droplet”, which can be interpreted as a bulk volume of the dispersed-phase species.

The subscripts B, S for $V_{B,S}$ and $R_{B,S}$ can be taken to denote “balance” (between osmotic and Laplace pressures in a drop) and “stability” (in the sense of Kabalnov et al[3]). However, in view of the thermodynamic discussion, it might be better to interpret them as “binodal” and “spinodal”. Indeed, depending upon the value of V_0 , any monodisperse distribution lies in one of three possible regimes: see figure 3. In regime I, the emulsion is fully stable under coarsening dynamics (though not, of course, under coalescence). In regime II it is metastable. In regime III it is locally unstable and will coarsen immediately. The metastable region II is both mathematically and physically analogous to that between the binodal and the spinodal lines governing phase coexistence in a binary fluid.

4.3 Kinetic Interpretation

The above thermodynamic argument is quite formal, so it is useful to interpret it in kinetic terms. Consider a monodisperse distribution which is in equilibrium with its “vapour” (*i.e.*, the dissolved fraction of the dispersed-phase species). Let the radius of all but one droplet be (say) $R_0 < R_S$, but suppose a single larger droplet is present, of radius R . The growth of this droplet is determined by whether $C(R, \eta)$ is larger or smaller than \bar{c} . Since the remaining droplets are in equilibrium, \bar{c} will be equal to

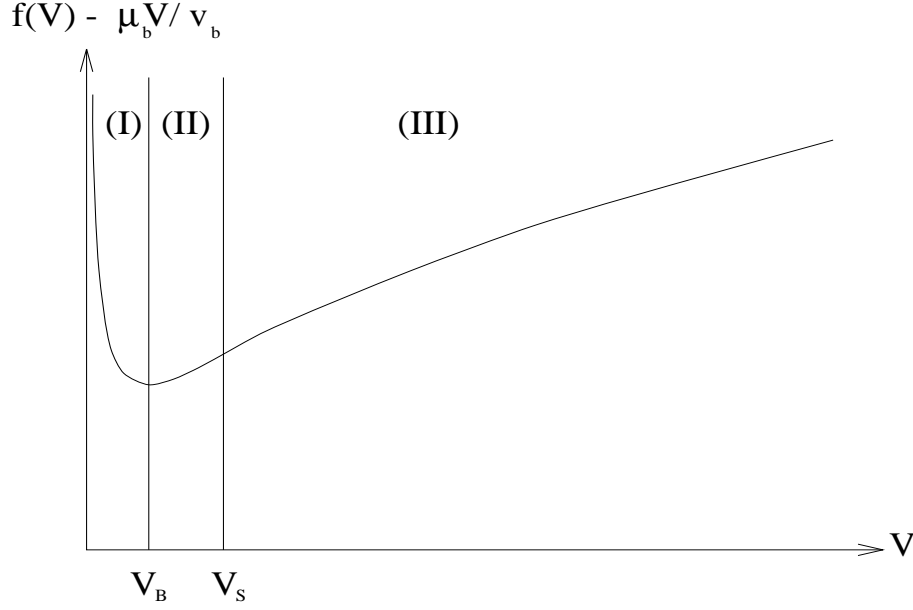


Figure 3: The three different stability regimes.

$C(R_0, \eta)$. Now consider the concentration of dispersed-phase species $C(R, \eta)$ at the surface of the anomalously large droplet (see figure 4).

Distributions in regime II have $R_B < R_0 < R_S$ and an average concentration of disperse phase $\bar{c}(R_0, \eta) > C(\infty, 0)$. Hence if a perturbed droplet is sufficiently large, its surface concentration will be below the ambient level (see figure 4) and the droplet will grow as a result of diffusive flux through the continuous phase, at the expense of smaller droplets. Distributions in regime I ($R_0 < R_B$) have $\bar{c} < C(\infty, 0)$ and there is no size of droplet larger than R_0 for which sustained growth is possible. Such a droplet will instead redissolve to rejoin the equilibrium droplets at size R_0 .

Returning now to distributions in regime II ($R_B < R_0 < R_S$), the critical size R_C above which a droplet will become unstable and start to grow is given by the larger root of $dR/dt = 0$, where dR/dt is given by Eq.17. This gives

$$R_C = R_\epsilon \left(1 - \left(\frac{R_B}{R_\epsilon} \right) - 2 \left(\frac{R_B}{R_\epsilon} \right)^2 - \dots \right) \quad (23)$$

where R_ϵ is as in Eq.15 and depends upon the supersaturation ϵ . Since the initial distribution of droplets is considered to be monodisperse with size R_0 and in equilibrium, then $dR/dt|_{R_0} = 0$ and R_ϵ may be determined as

$$R_\epsilon = \left(\frac{R_0^3}{R_0^2 - R_B^2} \right) \quad (24)$$

This suggests that, for a monodisperse initial state, the nucleation time for the coarsening process to begin (requiring nucleation of a droplet of size R_C) can become very large as R_0 approaches R_B . On the other hand, nucleation can occur immediately if there is any slight tail to the initial size distribution, extending beyond R_C .

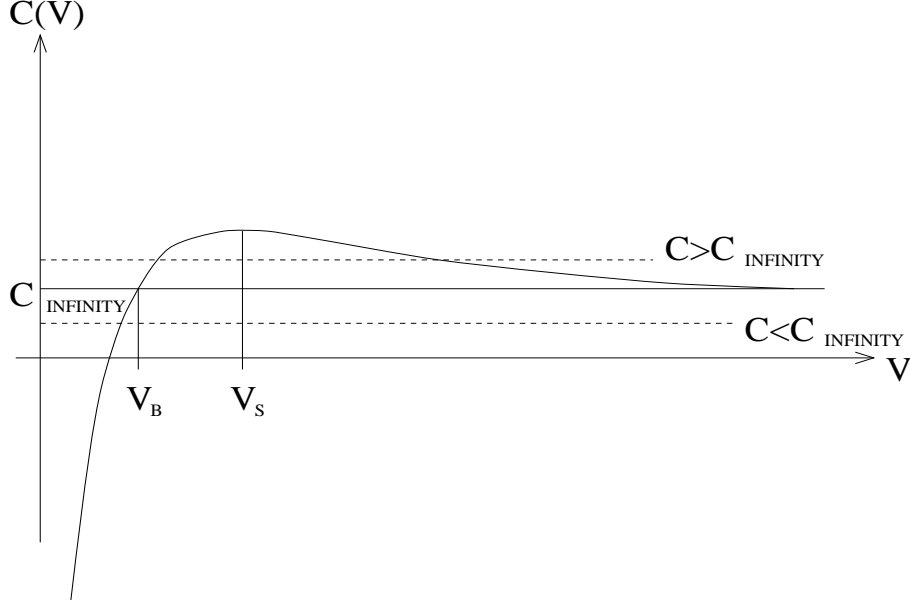


Figure 4: Variation in concentration of disperse phase at a droplets surface as a function of droplet volume.

The distinction between nucleation due to the existence of a tail in the initial size distribution which extends to abnormally large droplets, and nucleation resulting from fluctuations in growth rates, is similar to that between heterogeneous and homogeneous nucleation in conventional phase equilibrium. In this analogy the tail of the droplet size distribution (which may be negligible for thermodynamic purposes), provides “nucleation centres” which allow coarsening to begin.

4.4 Laplace and Osmotic Pressure Balance

The absolute stability requirement, $R_0 \leq R_B$ (Eq.22), is equivalent to requiring that $C(R_0, \eta) \leq C(\infty, 0)$. However, we have for an ideal trapped species

$$C(R, \eta) = C(\infty, 0) \left(1 + \frac{v_b}{k_B T} \left[\frac{2\sigma}{R} - \frac{\eta k_B T}{(4\pi/3)R^3} \right] \right) \quad (25)$$

Identifying $2\sigma/R$ with the Laplace pressure Π_L and $\eta k_B T / (4\pi/3)R^3$ with an osmotic pressure Π_{osm} of the trapped species, we see that the absolute stability condition may be written simply as

$$\Pi_L < \Pi_{osm} \quad (26)$$

or alternatively $2\sigma/k_B T < c_t R$ where $c_t = \eta/V_0$ is the concentration of trapped species in the dispersed phase. This means that if an emulsion is made from a dispersed phase of fixed c_t , a monodisperse emulsion will be fully stable only if the initial droplet size is sufficiently *large*. (The same applies to the metastability condition of Ref.[3].) This may be a rather unintuitive result; indeed, at fixed number of trapped particles η , as was used to discuss the $f(V, \eta)$ curves, stable emulsions arise only for *small* droplet

sizes ($R_0 \leq R_B$). However, for a fixed composition c_t , the value of η depends on R_0 ; and the important requirement is that the osmotic pressure (which inhibits coarsening) of an initial droplet exceeds its Laplace pressure (which drives it). At given c_t this is true only for large enough droplets.

4.5 Stability of Polydisperse Emulsions

The criterion discussed above for full stability can be extended to the polydisperse case. Let us first consider the case where the initial state contains droplets with variable sizes V_0 , but exactly the same η . This system will again find its equilibrium state at fixed total number of droplets n_0 and fixed volume fraction ϕ , which now obeys

$$\phi = n_0 \bar{V} \quad (27)$$

with \bar{V} the mean initial droplet volume. By again ignoring the entropy of mixing of the droplets (treating them as macroscopic objects), we see that the thermodynamic arguments developed in Section 4.1 for equilibrium at fixed droplet number apply without modification to this type of polydispersity. Therefore, the ultimate behaviour is found simply by substituting \bar{V} for V_0 in our previous discussion. Thus the criterion for full stability in this case is $\bar{V} \leq V_B$. It is also clear that in the stable regime the droplet distribution will evolve under the evaporation/condensation dynamics into a monodisperse one, whatever its initial polydispersity. This contrasts with the other regimes, where the final state will again have density n_0 of monodisperse droplets, but of size R_B and in coexistence with an “infinite droplet” containing the excess amount of dispersed phase ($n_0(\bar{V} - V_B)$) not residing in finite droplets.

The situation when η is not the same for all droplets is more complex. To find a stability condition for this case, we consider first a more formal argument which reproduces the above result for a single η . If the emulsion is unstable, we expect that at long times the size distribution will split into a “coarsening part” and a “stable part”. As equilibrium is approached, the coarsening part has some average size \bar{V}_c which tends to infinity at long times. This requires that $\epsilon \rightarrow 0$, which in turn means that the stable part of the distribution is necessarily monodisperse, and of droplet size $V \rightarrow V_B$. (This corresponds to the coexistence condition between finite and an infinite droplet mentioned previously.)

Let n_0 , n_s and n_c be respectively the number densities of all the droplets in the system, of those in the “stable part” and of those in the “coarsening part” of the distribution; clearly $n_0 = n_s + n_c$. Then as the system tends to equilibrium, the conservation of ϕ (which we define to include the trapped species) requires

$$n_0 \bar{V} = n_s V_B + n_c \bar{V}_c \quad (28)$$

and hence

$$n_0(\bar{V} - V_B) = n_c(\bar{V}_c - V_B) \quad (29)$$

So if $V_B \geq \bar{V}$, then $0 \geq n_c(\bar{V}_c - V_B)$; but since $\bar{V}_c > V_B$, then $n_c = 0$ and a coarsening part of the distribution cannot exist in this case.

Now we consider the more general situation where there is polydispersity, not only in the initial droplet size, but also in the quantity η of trapped species present in the initial droplets. Let $n(\eta)$, $n_s(\eta)$ and $n_c(\eta)$ be the number densities of droplets which

contain η trapped particles in the full distribution, and in its stable and coarsening parts respectively. As the system tends to equilibrium the conservation of ϕ and $n_0 = \int n(\eta) d\eta$ now requires

$$\int n(\eta) \bar{V} d\eta = \int n_s(\eta) V_B(\eta) d\eta + \int n_c(\eta) \bar{V}_c(\eta) d\eta \quad (30)$$

$$n_s(\eta) + n_c(\eta) = n(\eta) \equiv n_0 p(\eta) \quad (31)$$

where $p(\eta)$ is the probability of a given droplet having η trapped particles (which is time-independent). Hence

$$\begin{aligned} n_0 \bar{V} = & n_0 \int p(\eta) V_B(\eta) d\eta \\ & + \int n_c(\eta) (\bar{V}_c(\eta) - V_B(\eta)) d\eta \end{aligned} \quad (32)$$

which may be rewritten as

$$n_0 (\bar{V} - \langle V_B(\eta) \rangle_\eta) = \int n_c(\eta) (\bar{V}_c(\eta) - V_B(\eta)) d\eta \quad (33)$$

So if $\bar{V} \leq \langle V_B(\eta) \rangle_\eta$, then

$$0 \geq \int n_c(\eta) (\bar{V}_c(\eta) - V_B(\eta)) d\eta \quad (34)$$

but since $\bar{V}_c(\eta) > V_B(\eta)$, then $n_c(\eta) = 0$ for all η , and no coarsening part of the distribution can exist.

In summary, a condition which is sufficient to ensure the full stability of emulsions with an arbitrary initial distribution of sizes V and trapped species η is:

$$\bar{V} \leq \langle V_B(\eta) \rangle_\eta \quad (35)$$

where $\bar{V} = \phi/n_0$ and $V_B(\eta)$ is as defined in Eq.22: $V_B(\eta) = (4\pi/3)^{1/2} (\eta k_B T / 2\sigma)^{3/2}$. The assumptions behind this result are: (i) the trapped species has zero solubility in the continuous phase and forms an ideal solution in each droplet; (ii) coalescence is strictly absent; and (iii) the solubility of the main dispersed-phase species is nonzero (so that diffusion can occur) but small enough that it contributes negligibly to ϕ . Subject to these, it is a rigorous result. It is easily established, using arguments that parallel those of Section 4.1, that condition Eq.35 is not only sufficient for full stability but also necessary, in the sense that any distribution which does not satisfy Eq.35 can lower its free energy at fixed droplet number by a nucleated (if not a spinodal) coarsening process. As noted in Section 4.2 for the monodisperse case, for an emulsion which is only slightly unstable and whose size distribution does not have a tail extending to large droplets, the nucleation time before coarsening begins may be very long. If there is a tail, a long induction time is not expected.

Notice that our rigorous condition Eq.35 involves calculating $\langle V_B(\eta) \rangle_\eta$ by averaging over the probability distribution of the trapped species. This quantity is not the same as $V_B(\langle \eta \rangle)$; indeed for $\alpha \geq 1$ one has the general inequality

$$\int_0^\infty \eta^\alpha p(\eta) d\eta \geq \left(\int_0^\infty \eta p(\eta) d\eta \right)^\alpha \quad (36)$$

Since $V_B \sim \eta^{3/2}$ ($\alpha = 3/2$) we find that $\langle V_B(\eta) \rangle_\eta \geq V_B(\langle \eta \rangle)$. Hence the approximate stability requirement $\bar{V} \leq V_B(\langle \eta \rangle)$, based on the *mean* trapped particle number, underestimates the maximum initial droplet size. Accordingly this condition is sufficient, but not necessary, to ensure full stability.

4.6 The Metastable Regime (II)

For a polydisperse system the condition for full stability is clear (see above), whereas that for metastability is less obvious. Even when all droplets have the same η , metastability may depend on the details of the initial droplet size distribution. Certainly, if this has no upper limit (*i.e.*, there is a finite density of droplets above any given size), then the largest droplets will serve as nuclei for coarsening. As a qualitative rule, one can apply the argument of Section 4.3 in a mean-field approximation, whereby an anomalously large droplet is considered to be exchanging material with a set of others, which for simplicity we treat as having a single size \bar{V} . This enables a critical radius R_C to be estimated from Eq.23 by replacing the length scale R_ϵ with

$$R_\epsilon \simeq \left(\frac{3}{4\pi}\right)^{1/3} \left(\frac{\bar{V}_0}{\bar{V}_0^{2/3} - \bar{V}_B^{2/3}}\right) \quad (37)$$

As before, if the initial size distribution contains *any* droplets larger than R_C , coarsening can be expected.

If η varies between droplets, things are still more complicated, since nucleation is likely to involve droplets of larger than average η , as well as larger than average size. Although we still expect three regimes (fully stable, metastable and unstable) corresponding to those discussed in Section 4.3 for the monodisperse case, the boundary between the metastable and unstable regimes may have a complicated dependence on the initial distribution of droplets and trapped species. This contrasts with the very simple criterion for full stability, Eq.35 which applies for arbitrary initial conditions.

Note that the dynamics we propose for nucleation in the metastable region is peculiar to emulsions. For example, Reiss and Koper[8] discussed the equilibrium of a single drop within a uniform environment at fixed supersaturation. They concluded that for their problem nucleation dynamics were likely to be extremely slow, and deduced a criterion for stability corresponding to that given by Kabalnov et al. [7]. This does not contradict our own conclusions, because Reiss and Koper consider a *single drop* as opposed to a population of droplets. For an emulsion in regime II, only the largest drop present need exceed the nucleation threshold to initiate coarsening, and in many cases a large enough droplet would be present in the initial droplet size distribution. What is more, in a real emulsion with finite volume fraction, variations in the local environments experienced by individual droplets will be a source of dynamical fluctuations which may far exceed the purely thermal fluctuations considered in Ref.[8].

In summary, the stability conditions for a single droplet, and a population of droplets, are very different. We suspect that, even in a nominally monodisperse emulsion, nucleation rates are generally not negligible, and hence that the only reliable criterion for stability is the one we have given in section 4.5.

4.7 Other Equations of State

The thermodynamic arguments of Sections 4.1 and 4.2 generalise readily to an arbitrary equation of state for the trapped species. Indeed, for the case where η is the same in all droplets, one need only replace Eq.20 with,

$$f(V, \eta) = \mu_b V / v_b + 4\pi\sigma(3V/4\pi)^{2/3} + f_t(V, \eta) \quad (38)$$

where $f_t(V, \eta)$ is the free energy of η trapped particles in volume V and could include arbitrary interactions between these. If all droplets have the same η , the condition for stability remains that $\bar{V} \leq V_B$ where $V_B(\eta)$ is the droplet size corresponding to the absolute minimum of $f(V, \eta) - \mu_b V/v_b$. For such droplets, the osmotic pressure $(-\partial f_t/\partial V)_\eta$ is again in exact balance with the Laplace pressure. The metastability criterion is again that $f(V, \eta)$ has positive curvature. For the case where η is not the same for all droplets, the full stability criterion is again Eq.35.

A complication arises if the interactions between the trapped species are attractive. Reiss and Koper[8] pointed out that in this case a third, unstable fixed point can exist at a size smaller than V_B . They also correctly point out that such an attraction is likely to cause phase separation within droplets. The latter occurs whenever $f_t(V, \eta)$ has negative curvature (with respect to V at fixed η); the form of $f_t(V, \eta)$ in Eq. 38 must then be modified to reflect the internal phase separation, and any negative curvature regions will then be replaced by zero-curvature ones (corresponding to tie lines). In this case, because of the surface tension contribution in Eq.38, there can arise an additional minimum in $f(V, \eta) - \mu_b V/v_b$ which could lead, for example, to stable bidisperse emulsions for some range of initial conditions. The same can arise without intra-droplet phase separation, if $f_t(V, \eta)$ has a small enough positive curvature for this to be outweighed by the negative contribution from the surface tension term in Eq.38. We leave a detailed discussion of these cases for future work.

These results are sufficient, for example, to deal with the case of a distribution containing trapped salt (where $f_t(V, \eta)$ can be approximated by, say, the Debye Hueckel equation of state [22]) which is of interest in meteorological as well as emulsion stability contexts [11, 12, 13, 14, 15].

In the case of repulsive interactions, at least, our stability condition Eq.35 is also easily generalised to a situation in which there is more than one trapped species. Letting η_i be the number of particles of the i th species trapped within a droplet, then the condition for stability generalises to

$$\bar{V} \leq \langle V_B(\eta_1, \eta_2, \dots) \rangle_{\eta_1, \eta_2, \dots} \quad (39)$$

where $V_B(\eta_1, \eta_2, \dots)$ is the droplet size corresponding to the absolute minimum of $f(V, \eta_1, \eta_2, \dots) - \mu_b V/v_b$. A proof of this generalized stability condition follows that given in Section 4.5, with the single variable η replaced by the list of variables η_1, η_2, \dots

So far, we have not considered explicitly the role of surfactant (which is usually present to prevent droplet coalescence in emulsions), tacitly assuming that this merely alters the constant value of σ , the surface tension. For a surfactant that is insoluble in the continuous phase, this surface tension will itself be a function of droplet size. We do not treat this case further, but note that it could be included in Eq.38 by replacing the term in σ with a suitable “surface equation of state” for the trapped surfactant. The same applies to bending energy terms which could be significant for extremely small droplets.

4.8 Behaviour when the “trapped” phase is partially soluble

Throughout the above we have treated the trapped species as entirely confined in the emulsion droplets. In this Section we briefly consider what happens if this third species is very slightly soluble. (For simplicity we treat η as the same for all droplets.) Our

previous classification into regimes I, II and III, though no longer strictly applicable, remains a guide to the resulting behaviour. The discussion that follows is related to that of Kabalnov et al.[7].

Recall that for entirely trapped species, the unstable regime (III) is characterised by the evolution of a bimodal distribution of droplet sizes, in which the larger droplets coarsen by the Lifshitz–Slyozov mechanism, while the smaller droplets adopt a size in equilibrium with the larger drops which approaches V_B as coarsening proceeds. (This scenario is examined in more detail in Section 5 below.) If the trapped phase is now made slightly soluble, the larger drops will, as before, coarsen at a rate determined by the transport of the majority (more soluble) dispersed phase. However, the small droplets that remain cannot now approach a limiting size, but will themselves evaporate at a much slower rate governed by the transport of the “trapped” species. Therefore, in the unstable regime, a two-stage coarsening is expected. In the fully stable regime (I), on the other hand, the first of these processes (rapid coarsening of the larger droplets) is switched off. The droplet size distribution has a single peak, which in the fully insoluble case will approach a delta function at the initial mean size. However with slight solubility coarsening will occur via the Lifshitz–Slyozov mechanism, but only at a slower rate controlled by the transport of the less soluble species. The behaviour in the metastable regime (II) is complex[7], possibly characterised by a “crossover” from coarsening controlled by the less soluble component to coarsening controlled by the more soluble component, and we do not pursue it here.

For a slightly soluble trapped species, the best prospect for stability is always to avoid the *rapid* coarsening process associated with the transport of the more soluble dispersed phase component. Since there is always *some* part of the size distribution that coarsens at the slower rate set by the trapped species, the requirement is satisfied so long as the size distribution remains single-peaked at all times. In Appendix A we show that a sufficient condition for such behaviour is:

$$\overline{V}(0) \leq V_B(\overline{\eta}(0)) \quad (40)$$

where $\overline{\eta}(t)$ is the average number of trapped species in a droplet at time t . Since $V_B(\overline{\eta}(0)) \leq \overline{V}_B(\eta(0))$, this condition is less easily satisfied than our absolute stability condition, Eq.35, which applies for the case of entirely trapped species. Note, however, that although this condition is sufficient, we have been unable to find a necessary condition. In other words, it is possible that some systems will not satisfy Eq.40 but will nonetheless coarsen only slowly. The derivation[20] of Eq.40 requires $V_B(\eta)$ to increase faster than linearly with η ; this is valid for ideal mixtures and most other systems (perhaps excluding any in which interactions between the trapped species are attractive; see Section 4.7).

5 Coarsening Dynamics When a Trapped Species is Present

5.1 The Physics of Coarsening

We now consider conditions in which the requirement for stability, Eq.22, is not satisfied. For simplicity we take the case where all droplets have the same number of trapped

particles η . We also assume that any nucleation event required has taken place, and study the resulting coarsening process at late times. This entails small supersaturation ϵ . Throughout this Section we work in the scaled variables R' , R'_B and t' defined in sections 2 and 3, although the primes are omitted for convenience.

In the unstable case, as mentioned in Section 3, the equation for static equilibrium (zero growth) of a given droplet, $U(R, \epsilon) = 0$, has both a stable fixed point close to the balanced droplet size ($R \sim R_B$) and an unstable one at $R \sim 1/\epsilon$. The latter will lead to coarsening. The following arguments suggest that the presence of the additional, stable fixed point influences the coarsening dynamics only in a rather simple way. At long times, the main role of a population of stable droplets ($R \sim R_B$) is to effectively exclude a finite proportion of the dispersed phase from the coarsening process. The remaining part, whose volume fraction ϕ is effectively reduced, then coarsens almost normally.

To see this, we first expand $U(R, \epsilon)$ for small $R - R_B$ and small ϵ to obtain (in reduced units)

$$U(R) = \epsilon/R_B - (R - R_B) \left(\frac{2 + \epsilon R_B}{R_B^3} \right) \quad (41)$$

with a root $U = 0$ at

$$R_T(t) = R_B + \epsilon(t) \left(\frac{R_B^2}{2} \right) + O(\epsilon^2) \quad (42)$$

At late times ϵ will be small and therefore, according to Eq.41, the size of any droplet in the neighbourhood of R_B relaxes exponentially toward $R_T(t)$ with a fixed decay rate $2/R_B^3 + O(\epsilon)$. At long times, this process will be rapid compared to any coarsening of droplets of size $R \gg R_B$; hence any non-coarsening part of the droplet distribution comprises an effectively monodisperse population of radius $R_T(t)$ obeying Eq.42. Put differently, $R_T(t)$ is *determined* by ϵ , because the non-coarsening droplets are in local equilibrium with the ambient supersaturation at all times.

Now consider drops with size $R \sim 1/\epsilon$, in the neighbourhood of the second zero of $U(R, \epsilon)$ (this is the unstable fixed point of the growth equation at given ϵ). Expanding $U(R, \epsilon)$ in R about $R = 1/\epsilon$ we find

$$U(R) = (R - 1/\epsilon)\epsilon^3 + R_B^2\epsilon^4 \quad (43)$$

with a root

$$R_L(t) = 1/\epsilon - \epsilon R_B^2 \quad (44)$$

Accordingly, drops with $R(t) > R_L \sim 1/\epsilon$ will grow, lowering the supersaturation ϵ in the system. As this proceeds, the monodisperse small droplets ($R = R_T(t)$) will shrink slightly to remain in equilibrium with the current supersaturation. If one neglects this last effect, these droplets can play no role, at late times, other than to remove from the coarsening process an amount of material $n_0 V_B$ corresponding to that required to produce a stable monodisperse trapped emulsion in equilibrium with an infinite droplet. The excess material $n_0(V_0 - V_B)$ then becomes concentrated in fewer, larger droplets as coarsening proceeds by (essentially) the usual Lifshitz-Slyozov mechanism. This scenario is confirmed in the following Section, where we obtain an asymptotic solution for the coarsening behaviour.

5.2 Asymptotic Analysis

Following Lifshitz and Slyozov [1] we assume a continuous distribution of droplet sizes $n(R, t)$, with $n(R, t) dR$ representing the number density of droplets of radius $(R, R + dR)$, at time t . Since droplets of finite size cannot suddenly appear or disappear, the conservation of flux through droplet size space requires [1, 18]

$$\frac{\partial n(R, t)}{\partial t} = - \frac{\partial(n(R, t)U(R, \epsilon))}{\partial R} \quad (45)$$

Conservation of the volume of dispersed phase species requires that

$$\frac{1}{C_\infty v_b} \int_0^\infty \frac{4\pi}{3} R^3 n(R, t) dR + \epsilon = \epsilon_0 \quad (46)$$

where $\epsilon = (\bar{C} - C_\infty)/C_\infty$ is the degree of supersaturation and ϵ_0 its initial value.

Taking $R_T(t)$ and $R_L(t)$ as the two roots of $U(R, \epsilon) = 0$, as defined above, we now seek asymptotic solutions of the form

$$n(R, t) = A_T(R_T) f_T(R/R_T) + A_L(R_L) f_L(R/R_L) \quad (47)$$

where f_T and f_L are two different scaling functions. That is, we assume (see figure 5) that at late times the size distribution splits into two populations, each of fixed shape in terms of an appropriate reduced size variable, and each with some time-dependent amplitude A .

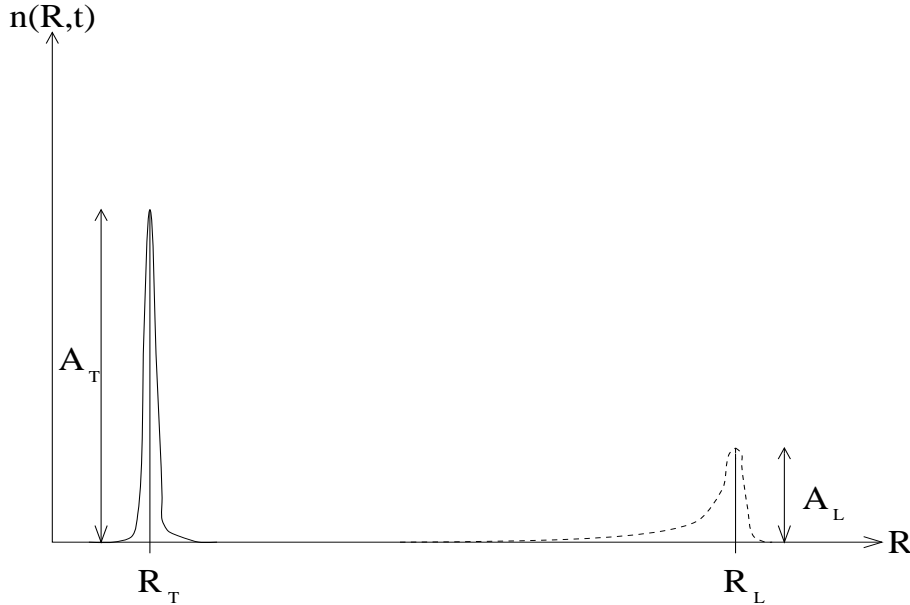


Figure 5: Approximating $n(R, t)$ by functions centred on R_T and R_L .

These two distributions are now assumed to *separately* obey Eq.45 for conservation of flux through droplet size space. This separation is valid so long as there is no significant range of sizes for which both populations overlap – which is increasingly true

at late times. However, the two populations do interact via the supersaturation ϵ . We first solve $U(R_L, \epsilon) = 0$ for $\epsilon(R_L(t))$ to obtain

$$\epsilon = \frac{1}{R_L(t)} \left(1 - \frac{R_B^2}{R_L(t)^2} \right) \quad (48)$$

and note that, because of this equation, terms in ϵ and terms in $1/R_L$ are of the same order. In what follows we take the long time limit and therefore write $\epsilon = 1/R_L + O(1/R_L^3)$. We then impose conservation of volume fraction, and of the total number of droplets (n_0), to obtain A_T and A_L . This is done explicitly in Appendix B and yields

$$A_T = \frac{n_0}{R_T(\epsilon)} + O(\epsilon^3) \quad (49)$$

and

$$A_L = \frac{\epsilon_0 - n_0(4\pi/3)R_B^3/(C(\infty)v_b)}{(4\pi/3)B_{0L}R_L(t)^4} - O(\epsilon^5) \quad (50)$$

where B_{0L} is a moment of the scaling function f_L defined in Appendix B.

Eq.45 is then expanded in powers of R_L retaining only the lowest order terms in $1/R_L$ (or equivalently, the lowest order terms in powers of ϵ). As shown in Appendix C, this results in $R_L(t) = (3\gamma t)^{1/3}$ and

$$\begin{aligned} \left[4f_L + Z_L \frac{\partial(f_L(Z_L))}{\partial Z_L} \right] = & \gamma \left[f_L \left(-\frac{1}{Z_L^2} + \frac{2}{Z_L^3} \right) \right. \\ & \left. + \frac{\partial(f_L(Z_L))}{\partial Z_L} \left(\frac{1}{Z_L} - \frac{1}{Z_L^2} \right) \right] + O(\epsilon) \end{aligned} \quad (51)$$

where $Z_L = R/R_L(t)$. These equations are identical to those solved by Bray[18], resulting in the consistency requirement $\gamma = 4/27$, and the solution

$$f_L(Z_L) = \begin{cases} \frac{AZ_L^2 \exp\left(\frac{-3}{3-2Z_L}\right)}{(3+Z_L)^{7/3}(3/2-Z_L)^{11/3}} & 0 \leq Z_L < 1.5 \\ 0 & 1.5 \leq Z_L \end{cases} \quad (52)$$

where A is a constant which is determined by the condition $\int f_L(Z_L) dZ_L = 1$.

The above argument shows that the equation of motion for R_L is exactly the same as in a standard coarsening problem (with no trapped species)[18], to the leading order in small ϵ . Accordingly the solution for $R_L(t)$, which involves seeking a specific γ for which the scaling distribution remains self-consistent in the long-time limit, is also the same. The only difference is in the *amplitude* A_L which, as shown in Eq.50, has, to the leading order in ϵ been shifted by a constant amount corresponding to a reduction in ϵ_0 . In other words, in the long time limit the large droplets behave *precisely*[23] as they would for an emulsion with no trapped species but a reduced initial volume fraction $n_0(V_0 - V_B)$. (Obviously, the latter is assumed positive; otherwise the emulsion is stable and will not coarsen.)

6 Possible Applications

6.1 Optimal Sizing of Emulsions

The use of “trapped”, or less soluble species to stabilize emulsions is widespread in industry [24]. Such emulsions can be prepared mechanically with various average droplet sizes. Let us assume that any trapped species is dissolved at uniform concentration c_t through the dispersed phase material. As explained in Section 4.4, to form a stable emulsion one must ensure that the initial droplet size is sufficiently *large*. Roughly speaking, this ensures that the typical Laplace pressure $2\sigma/R$ is smaller than the osmotic pressure $c_t k_B T$. (The quantitative version of this, applicable to any initial size distribution, is Eq.35.) Clearly, it is important to resist the temptation to make the initial emulsion too fine (which in ordinary emulsions might be expected to delay coarsening for the maximum possible time). In practice, the need to avoid sedimentation (and perhaps coalescence, which we have neglected) may set an optimal initial size close to, but above, the absolute stability threshold, Eq.35. For the reasons discussed in Section 4, the weaker “spinodal” condition[7] Eq.21, even for a nominally monodisperse initial state, cannot guarantee stability.

6.2 Reversing the Coarsening Process

Consider a situation where an emulsion is prepared in an unstable state (for example by mechanical agitation) and then starts to coarsen. We now ask what will happen if, after some time interval, a large number of small droplets (containing a trapped species) are added to the emulsion, causing the stability condition $\bar{V} \leq \langle V_0(\eta) \rangle_\eta$ to become satisfied for the system as a whole. According to the arguments of Section 4.5, the emulsion is now unconditionally stable. Therefore it will not coarsen further. What is more, for a given total volume fraction ϕ and a given population of trapped species, the final state of the system is the unique one in which droplets of all η have a common chemical potential for the (mobile) disperse-phase species. Thus the addition of the small droplets will not only prevent further coarsening, but will in general cause previously coarsened droplets to *redissolve*. Indeed, if there are no trapped species in the initial unstable droplets, these will evaporate completely, and their material will be entirely absorbed by the added droplets[25]. A formal proof of these remarks, following the lines of Section 4.5, is left to the reader.

In principle, the coarsening process can be reversed even when it is complete. For example, a system of small oil-in-water emulsion droplets with trapped species present can, by the evaporation-condensation mechanism, take up oil from an excess bulk phase of pure oil. If the stability condition $\bar{V} \leq \langle V_0(\eta) \rangle_\eta$ is met by the system as a whole[26], the bulk phase of oil will disappear entirely (though obviously this process may be slow in practice). Like the rest of our conclusions, this one applies only if both coalescence, and diffusion of the trapped species through the continuous phase, are strictly negligible. With these assumptions, we may minimize the free energy with the constraint of fixed trapped species in each drop; the above result for the equilibrium state follows immediately.

6.3 Formation of Mini-emulsions by Shrinking

“Mini-emulsions”, comprised of droplets with radii of between 50 and 150 nm, have many potential uses in industrial and pharmaceutical applications[24]. However their

formation by traditional mechanical methods, where droplets are formed by strongly shearing the ingredients, is limited by the high energy required by the process[27], and the difficulty of getting a uniform droplet size. An alternative route is to create an emulsion of relatively large drops (whose size is also more controllable) and then “shrink” them to the required, smaller size. The following describes a non-mechanical method which would allow this to be done.

Consider a situation in which a bulk reservoir of the dispersed-phase species (say, oil), containing trapped species at concentration c_b , is placed in contact with a stable emulsion of oil droplets (in water, say) each containing η molecules of the trapped species (see figure 6). This system is then allowed to reach equilibrium under the evaporation-condensation mechanism. (To speed the process, some gentle agitation of the emulsion might be desirable.)

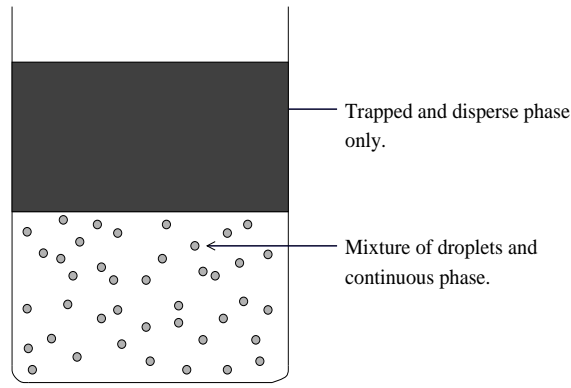


Figure 6: Droplets shrink to attain a stable size, which is in equilibrium with an excess bulk phase that also contains a trapped species.

A final state of equilibrium will be reached when the chemical potential of the dispersed phase species in the emulsion equates to that in the bulk. This requires

$$\Pi_{osm}^{bulk} = \Pi_{osm}^{drop} - \Pi_L \quad (53)$$

where $\Pi_{osm}^{bulk,drop}$ are the osmotic pressures of trapped species in the bulk and droplets and Π_L is the Laplace pressure in the droplets. For ideal solutions this condition reads

$$c_b = \frac{\eta}{(4\pi/3)R^3} - \frac{2\sigma}{Rk_B T} \quad (54)$$

which is an equation for the final droplet size R . By increasing c_b the final droplet size can be made as small as one wishes: effectively the oil can be “squeezed out” of the emulsion by the osmotic action of the trapped species, now present in the bulk oil phase at higher concentration. (This contrasts with the last example in Section 6.2, where a bulk phase, containing no trapped species, could be entirely absorbed by the emulsion droplets.) Once the desired size of mini-emulsion is reached, it can be removed and will remain stable.

Note that, because the trapped species is insoluble in the continuous phase (water in this example), there is no need for a semipermeable membrane to prevent its

transfer between the bulk oil phase and the emulsion droplets. Therefore, in practice, a more rapid exchange equilibrium might be reached if the “bulk” oil phase instead took the form of large macroemulsion droplets which can later be separated out easily by sedimentation. Moreover, there is no need for the trapped species in the bulk oil phase, and the trapped species in the mini-emulsion droplets, to be identical; so long as both are insoluble in water, the same condition for osmotic equilibrium will apply. Therefore one can “shrink” an emulsion containing an expensive trapped species (such as a fragrance or drug) by contacting it with a cheap polymer solution.

The shrinking process should not only achieve small droplet sizes, but may also allow one to reach concentrations of the trapped phase that would be unattainable by normal means. For example, by making an emulsion of dilute polymer solution and then shrinking the droplets, it may be possible to achieve within each droplet a highly concentrated polymer solution, too viscous to be dispersed mechanically in its own right.

These ideas may be relevant to various encapsulation technologies. Obviously, the designation of “oil” and “water” in the above is arbitrary and these could be any two phases. We have assumed throughout that coalescence is negligible, which is commonly the case for oil-in-water emulsions so long as they contain a surfactant (typically ionic), to give a surface repulsion between droplets. The presence of the surfactant should not alter our arguments, so long as it is soluble enough in the continuous phase that the surface tension σ does not vary between droplets. In principle, for small enough mini-emulsions, the surfactant could also give rise to significant bending energy terms in the free energy of a droplet, which could be included if required (see Section 4.7).

7 Conclusions

It has long been known that emulsions containing a sufficiently high concentration of a trapped phase will not coarsen via the Lifshitz-Slyozov[1] mechanism (Ostwald Ripening). For practical purposes it is clearly important to know what is “sufficiently high” in this context; this information can allow stable emulsions to be designed, rather than formulated by trial and error.

In this work we have provided a general condition (Eq.35) which (in the absence of droplet coalescence) will guarantee stability against coarsening, for emulsions of arbitrary polydispersity in both initial droplet size and composition. The remarkable simplicity of our result stems from a correspondence between the thermodynamics of emulsions at fixed droplet number and the equilibrium among multiphase fluids (Section 4.1).

Although presented for an ideal solution of trapped species, our condition may be generalised to an arbitrary equation of state (see Section 4.7). In fact though, for typical parameters ($\sigma \simeq 10^{-1} \text{N m}^{-1}$, $R_0 \simeq 1 \mu\text{m}$) stability can be achieved with trapped concentrations of order 10^{-2}M so that departures from ideality need not arise. An analogous condition (Eq. 40) was also found that ensures a relatively long-lived emulsion even when the “trapped” phase is slightly soluble.

In deriving Eq.35 (and its simplified form, Eq.22 for the monodisperse case) we took care to distinguish “nucleated” from “spinodal” coarsening. Eqn.35 rigorously identifies the boundary between fully stable emulsions of arbitrary initial polydispersity

(regime I) and emulsions that can lower their free energy by coarsening at fixed droplet number. The latter can be subdivided into two classes (regimes II and III). In regime II, coarsening can occur by nucleation. The nucleation can arise either because of variations in the local environments of droplets, or from the presence in the initial state of even a *single* pre-existing large droplet. We believe that the latter, in particular, can rarely be ruled out.

In contrast, spinodal coarsening (regime III) requires neither mechanism since typical droplets are locally unstable. We showed that for monodisperse emulsions, Eq.21 as proposed by Kabalnov et al.[7] actually identifies the onset of spinodal coarsening. If in general nucleated processes cannot be ruled out, condition Eq.21 is insufficient for stability.

The effect of trapped species on the dynamics of unstable, coarsening emulsions was also considered. It was found that coarsening would proceed precisely like that in an emulsion with no trapped species[1], but with a reduced initial volume fraction $n_0(V_0 - V_B)$.

We have emphasised that the emulsions evolution is driven by the competition between the osmotic pressure of the trapped species and the Laplace pressure of droplets. These principles are exploited in Section 6.3, where we describe non-mechanical methods which might allow the restabilization of a partially coarsened emulsion and the formation of stable emulsions consisting of droplets smaller than those attainable by traditional mechanical methods.

There is scope for further work in several directions. For example, it would also be interesting to consider further the detailed kinetics of emulsions in the metastable regime (II); these can be complex, especially if the “trapped” species is itself slightly soluble (Section 4.8). For practical purposes in designing emulsions, however, this regime is best avoided as we have emphasized above. Of greater technological importance is the case of emulsions which consist of multiple components of varying solubility. One would like criteria for the average droplet composition that will maximise such an emulsion’s lifetime. We hope to return to this issue in future studies.

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A Slow coarsening condition for a slightly soluble “trapped” species

In this Appendix we establish Eq.40, which is the condition that the size distribution remains single-peaked at all times, in a system where the trapped particles are slightly soluble.

We do this by considering the contrary case of a distribution which consists of both a rapidly coarsening and a quasi-stable part, with the rapid coarsening of the larger drops occurring at a rate determined by the transport of the most soluble component. As $t \rightarrow \infty$, the size V_L of the larger droplets becomes large, the supersaturation of the disperse phases will tend to zero, and the smaller drops will tend to sizes $V_B(\eta)$. Here η may now vary among droplets and with time.

The total number of droplets is no longer conserved but becomes time-dependent, and Eq.33 is replaced by

$$n(0)\overline{V}(0) - n(t)\overline{V}_B(t) = \int n_L(\eta, t)(\overline{V}_L(t) - V_B(\eta))d\eta \quad (55)$$

where $n_L(\eta, t)$ is the number of droplets at the larger size $V_L(t)$, and $\langle V_B(t) \rangle_\eta$ has been rewritten as $\overline{V}_B(t)$ for convenience. So if we can ensure that

$$\overline{V}(0) - \frac{n(t)\overline{V}_B(t)}{n(0)} \leq 0 \quad (56)$$

then $n_L(\eta, t) = 0$ and the distribution must be single-peaked.

Conservation of the less soluble components requires that

$$n(0)\overline{\eta}(0) = n(t)\overline{\eta}(t) \quad (57)$$

or

$$\frac{n(t)\overline{V}_B(t)}{n(0)} = \frac{\overline{\eta}(0)\overline{V}_B(t)}{\overline{\eta}(t)} \quad (58)$$

We next note that $V_B(0) = 0$ and assume that $V_B(\eta)$ is convex, as is the case for ideal phases where $V_B \sim \eta^{3/2}$. (This ensures that if $y_2 > y_1$, then $y_1 V_B(y_2) > y_2 V_B(y_1)$.) If so

$$\overline{V}_B(t) \geq V_B(\overline{\eta}(t)) \quad (59)$$

And

$$\overline{\eta}(0)\overline{V}_B(t) \geq \overline{\eta}(0)V_B(\overline{\eta}(t)) > \overline{\eta}(t)V_B(\overline{\eta}(0)) \quad (60)$$

To obtain the second inequality, we have again used the fact that $V_B(\eta)$ increases faster than linearly with η and also exploited the fact that $\overline{\eta}(t)$ increases with time. (The latter follows from the fact that the number of droplets present must decrease as time proceeds.) Hence $\overline{\eta}(0)\overline{V}_B(t)/\overline{\eta}(t) > V_B(\overline{\eta}(0))$ and

$$\overline{V}(0) - \frac{n(t)\overline{V}_B(t)}{n(0)} = \overline{V}(0) - \frac{\overline{\eta}(0)\overline{V}_B(t)}{\overline{\eta}(t)} < \overline{V}(0) - V_B(\overline{\eta}(0)) \quad (61)$$

So if $\overline{V}(0) \leq V_B(\overline{\eta}(0))$ then $\overline{V}(0) - n(t)\overline{V}_B(t)/n(0) < 0$ and $n_L(\eta, t) = 0$. Hence the distribution may only contain a single peak, and will coarsen at rate determined by the less soluble component.

B Determination of A_T and A_L

In this Appendix, we obtain results for the amplitudes A_T and A_L as defined in Section 5.2. These are determined by the constraints of conservation of volume fraction and conservation of the total number of droplets. We write $n(R, t) = n_T + n_L$, with $n_T = A_T f_T(R/R_T)$ and $n_L = A_L f_L(R/R_L)$. We then define f_T and f_L to be normalised so that $\int_0^\infty f_T(Z_T)dZ_T = \int_0^\infty f_L(Z_L)dZ_L = 1$, where $Z_T = R/R_T$ and $Z_L = R/R_L$. Conservation of total number of droplets then implies

$$A_T R_T + A_L R_L = n_0 \quad (62)$$

Defining $\int_0^\infty f_T Z_T^3 dZ_T / C_\infty v_b = B_{0T}$ and $\int_0^\infty f_L Z_L^3 dZ_L / C_\infty v_b = B_{0L}$, then conservation of volume fraction implies

$$\frac{4\pi}{3}(A_T R_T^4(\epsilon) B_{0T} + A_L R_L^4(t) B_{0L}) + \epsilon = \epsilon_0 \quad (63)$$

or

$$A_L R_L(t) = \frac{(\epsilon_0 - \epsilon) - B_{0T} A_T (4\pi/3) R_T(\epsilon)^4}{(4\pi/3) B_{0L} R_L(t)^3} \quad (64)$$

Substitution into Eq.62 for A_T then gives

$$A_T = \frac{n_0}{R_T(\epsilon)} - \frac{(\epsilon_0 - \epsilon) - B_{0T} A_T (4\pi/3) R_T(\epsilon)^4}{(4\pi/3) B_{0L} R_L(t)^3 R_T(\epsilon)} \quad (65)$$

which, to the order required, is Eq.49. Likewise for A_L we obtain

$$A_L = \frac{(\epsilon_0 - \epsilon) - n_0 B_{0T} (4\pi/3) R_T(\epsilon)^3}{(4\pi/3) B_{0L} R_L(t)^4} \quad (66)$$

Substituting Eq.42 for $R_T(\epsilon)$ and Eq.48 for $\epsilon(R_L)$ yields

$$A_L = \frac{\epsilon_0 - n_0 B_{0T} (4\pi/3) R_B^3}{(4\pi/3) B_{0L} R_L(t)^4} - \frac{(1 + (3R_B/2) B_{0T} (4\pi/3) R_B^3)}{(4\pi/3) B_{0L} R_L(t)^5} \quad (67)$$

Since Eq.41 determines that droplets in the neighbourhood of R_B will relax at an exponential rate towards R_T , f_T (which is normalized to unity) will converge at an exponential rate onto $f_T = \delta(Z_T - 1)$. Hence B_{0T} equals $1/(C(\infty)v_b)$ and A_L becomes

$$A_L = \frac{\epsilon_0 - (n_0 (4\pi/3) R_B^3)/(C(\infty)v_b)}{(4\pi/3) B_{0L} R_L(t)^4} - \frac{(1 + (3R_B/2) (4\pi/3) R_B^3)/(C(\infty)v_b)}{(4\pi/3) B_{0L} R_L(t)^5} \quad (68)$$

which to the required order is Eq.50.

C Determination of n_L

We have assumed that $n_L(R, t)$ satisfies (by itself) the continuity equation in droplet size space,

$$\frac{\partial n_L(R, t)}{\partial t} = - \frac{\partial (n_L(R, t) U(R, \epsilon))}{\partial R} \quad (69)$$

Writing $n_L(R, t) = A_L f_L(Z_L)$ we obtain

$$\frac{\partial (A_L f_L(Z_L))}{\partial t} = - \frac{\dot{R}_L}{R_L} Z_L A_L \frac{\partial (f_L(Z_L))}{\partial Z_L} + \frac{\partial A_L}{\partial t} f_L(Z_L) \quad (70)$$

Defining

$$K_1 = \frac{\epsilon_0 - n_0 (4\pi/3) R_B^3 / C(\infty) v_b}{(4\pi/3) B_{0L}} \quad (71)$$

and

$$K_2 = \frac{1 + (3R_B/2) B_{0T} (4\pi/3) R_B^3 / C(\infty) v_b}{(4\pi/3) B_{0L}} \quad (72)$$

then we find

$$\frac{\partial A_L}{\partial t} = -4 \frac{\dot{R}_L}{R_L} A_L - K_2 \frac{\dot{R}_L}{R_L^6} \quad (73)$$

So we obtain

$$\frac{\partial n_L(R, t)}{\partial t} = -A_L \frac{\dot{R}_L}{R_L} \left(4f_L + Z_L \frac{\partial(f_L(Z_L))}{\partial Z_L} \right) - K_2 \frac{\dot{R}_L}{R_L^6} f_L \quad (74)$$

We next write $\partial(n_L(R, t)U(R, \epsilon))/\partial R$ in terms of Z_L to obtain

$$\begin{aligned} \dot{R}_L R_L^2 (4f_L + Z_L \frac{\partial(f_L(Z_L))}{\partial Z_L}) + \frac{K_2 \dot{R}_L}{R_L^3 A_L} f_L = & \left[f_L \left(-\frac{1}{Z_L^2} + \frac{2}{Z_L^3} - \frac{4(R_\alpha/R_L)^2}{Z_L^5} \right) \right. \\ & \left. + \frac{\partial(f_L(Z_L))}{\partial Z_L} \left(\frac{1}{Z_L} - \frac{1}{Z_L^2} + \frac{(R_\alpha/R_L)^2}{Z_L^4} \right) \right] \end{aligned} \quad (75)$$

Expanding $1/(R_L^3 A_L)$ to lowest order in $1/R_L$ we obtain $K_2 \dot{R}_L / R_L^3 A_L \rightarrow K_2 \dot{R}_L R_L$; keeping only the leading terms on the right hand side we are left with

$$\begin{aligned} \dot{R}_L R_L^2 (4f_L + Z_L \frac{\partial(f_L(Z_L))}{\partial Z_L}) + K_2 \dot{R}_L R_L f_L = & \left[f_L \left(-\frac{1}{Z_L^2} + \frac{2}{Z_L^3} \right) \right. \\ & \left. + \frac{\partial(f_L(Z_L))}{\partial Z_L} \left(\frac{1}{Z_L} - \frac{1}{Z_L^2} \right) \right] \end{aligned} \quad (76)$$

Since the R.H.S. is a constant, then as $t \rightarrow \infty$ the L.H.S. must also approach a constant value. Trying $R_L = \Gamma t^\beta$ with Γ a constant, then

$$\dot{R}_L R_L^2 = \beta \Gamma^3 t^{3\beta-1} \quad (77)$$

and

$$\dot{R}_L R_L = \beta \Gamma^2 t^{2\beta-1} \quad (78)$$

Clearly both will tend to zero if $\beta < 1/3$, which would not correspond to a coarsening state. However if $\beta > 1/3$ then the L.H.S of the equation would diverge at late times. Hence $\beta = 1/3$, and as $t \rightarrow \infty$, $\dot{R}_L R_L \rightarrow 0$. Writing $\gamma = \Gamma^3/3$ then results in the same equation as that obtained and solved by Bray[18], namely Eq.51.

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